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Address inquiries to
Eastman Organic Chemicals Dept.
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Solvents for Spectrophotometry

By D. H. ANDERSON* and D. W. STEWART†

Solvents are needed for many purposes. They serve as reaction media, as reactants, and as reference standards for melting-point, boiling-point, and refractive-index determinations. They have many other applications.

Advances in spectrophotometry and the widespread acceptance of spectrophotometric techniques require the analytical chemist to maintain a supply of solvents that are spectrophotometrically "pure." The requirements of the analytical chemist are somewhat different from those of other chemists. For example, methanol used in synthesizing a methyl ester could contain small amounts of benzene and the organic chemist would, in most instances, not be at all concerned about the presence of this impurity. In ultraviolet absorption spectrometry, however, the presence of even 0.005 percent of benzene or other aromatic chemical would be a serious contaminant and would bar its use in some analytical work.

Carbon tetrachloride may contain chloroform and still be satisfactory as an extracting medium for fats or similar substances if the residue is to be measured gravimetrically. However, if the substance being extracted is to be identified or measured using infrared techniques, the presence of the chloroform, with its additional absorption bands, works a real hardship for the chemist.

If ultraviolet absorption measurements are to be made, ethanol denatured with methanol is a very acceptable solvent because both are very transparent in this region. The presence of the methanol may, however, cause difficulty in some infrared work.

In absorption spectrophotometry, solutions should have the following characteristics: (1) In the spectral region of interest, the solvent should have a minimum of absorption. The amount of absorption which can be tolerated depends upon the cell thickness to be used, and this depends, in turn, upon the concentration of solute and upon the extinction coefficient of the absorption band. (2) Solubility of the solute in the chosen solvent must be sufficiently great so that the absorption will be strong enough to measure with acceptable precision. In the case of low solubilities, increased cell thickness may compensate in part, but only to the extent that absorption by the solvent itself does not increase unduly. (3) The solution must not attack the materials of the absorption cell or the cell windows. In the infrared, where windows of the crystalline halides of sodium, potassium, thallium, or silver are generally used, this may be a serious problem.

The selection of solvents for use at

*Industrial Laboratory, Eastman Kodak Company, Rochester 4, New York.
†Research Laboratories, Eastman Kodak Company, Rochester 4, New York.

wavelengths in the visible region and in the ultraviolet down to about 200 millimicrons offers relatively little difficulty. In the ultraviolet region, the choice is not as wide as in the visible, but polar materials, such as water and the alcohols, supplement the nonpolar solvents, such as cyclohexane, 2,2,4-trimethyl pentane (iso-octane), and others. The chief question is frequently the lower limit of transparency or the "cutoff." The question of contamination may also be important because of the strong absorption which may be introduced by trace amounts of aromatic impurities.

Because of much more general absorption by solvents in the infrared region, and because of the further complication of attack on cell windows which may eliminate otherwise useful solvents, most of what follows will pertain to spectrophotometry at wavelengths longer than the visible.

From a simplified consideration of the process by which molecules interact with infrared radiation, it is clear that polar molecules will generally show strong absorptions. The number of such absorption bands for any substance will increase with increasing complexity in the molecule, and their position will depend, to a first approximation, on the masses of the atoms and on the strength of binding between them. Thus, for maximum transparency in the most used infrared region (from the visible to about 16 μ), the ideal solvent is nonpolar and will contain a minimum number of elements, all as heavy as possible, and all held together by bonds as weak as possible. From this standpoint, carbon disulfide and carbon tetrachloride approach the ideal, although both show a number of strong absorptions between 2 and 16 μ. Fortunately, these do not overlap seriously, so that the entire spectrum can be covered, using carbon tetrachloride up to approximately 7.6 μ, and carbon disulfide at longer wavelengths. Above 15 μ, a different choice of solvents is indicated for maximum transmission. Marrison (1) has examined between sixty and seventy liquids and recommends a number of them as completely transparent between 15 and 25 μ. These include carbon tetrachloride, tetrachloroethylene, *n*-hexane, *n*-heptane, and acetonitrile.

For materials with borderline solubility in the nonpolar solvents, the use of a mixture in which a minor component is used to solubilize the sample has proved useful. This technique has been reviewed by Ard and Fontaine (2), who have used a 0.5-2.5 percent solution of triethyl amine in carbon disulfide or carbon tetrachloride for dissolving organic acids. The resulting neutralization of the acid introduces some changes in the spectrum, but these would seldom prevent useful quantitative measurements.

For materials insoluble in nonpolar solvents, one can rarely find any two, or even three, polar liquids which will provide satisfactory solubility and transparency over the entire spectrum. Water can be used with silver chloride cell windows, but only in extremely thin layers because of its opacity. Other polar solvents may have regions of satisfactory transparency, but the position of these cannot be predicted easily, and they may be so narrow as to conceal completely the general nature of the solute's absorption spectrum. The situation is more favorable if a quantitative determination of one or more known components in the solution is desired, since the few wavelengths at which measurements must be made are known and solvents with suitable transmission characteristics can be selected by reference to a collection of solvent spectra. Torkington and Thompson (3) tabulate seventeen such spectra, with recommended regions of usefulness. Pristera (4) has collected more detailed spectrograms for twenty-four different solvents, and even more extensive private collections will be found in most infrared laboratories.

When the infrared spectrum of a solid is desired for qualitative identification, solvent difficulties may be avoided if a

suspension of crystal fragments dispersed by grinding in a medium such as refined mineral oil is used. Absorptions of the oil near 3.4, 6.8, and 7.2 μ are strong enough to mask the spectrum of the suspended solid, but other regions of the spectrum are relatively open. The use of perfluorokerosene eliminates these interferences, but the fluorocarbon is itself opaque above about 7.2 μ. Hexachlorobutadiene has also been suggested (5) as a useful mulling medium.

Difficulties in making reproducible mulls, and in measuring accurately the small thickness of cell in which they are usually examined, make quantitative studies with them somewhat difficult. A recently described technique (6) uses aluminum stearate as a dispersing agent. In some of the usual infrared solvents, such as carbon disulfide, a 1 percent solution of this agent will suspend, with grinding, about 1 percent of insoluble sample to form a suspension which is stable for 30 minutes or more, and which can be handled as a solution in liquid cells. The laws relating absorbance to cell thickness and concentration of solutions appear to be applicable to these suspensions.

When none of the solution or suspension techniques are adequate, and when the solid cannot be examined as a single crystal or as a film deposited by melting or evaporation from solution, the recently suggested high-pressure laminating or molding methods may be used. The sample is either pulverized and mixed with crystals of an alkali halide or silver chloride, and then pressed in vacuum (7, 8), or a pellet is pressed at high temperature between sheets of transparent material, such as mica, polyethylene, potassium bromide, or silver chloride (9). The method has been developed for certain specific applications, but should find wide use where limited solubility makes more conventional techniques unsatisfactory.

References

(1) Marrison, L. W., *J. Sci. Instruments*, **29**, 233 (1952).
(2) Ard, J. S., and Fontaine, T. D., *Anal. Chem.*, **23**, 133 (1951).
(3) Torkington, P., and Thompson, H. W., *Trans. Faraday Soc.*, **41**, 184 (1945).
(4) Pristera, F., *Appl. Spectroscopy*, **6**, 29 (1952).
(5) Ard, J. S., *Anal. Chem.*, **23**, 680 (1951).
(6) Dolinsky, M., *J. Assoc. Official Agricultural Chemists*, **34**, 748 (1951).
(7) Stimson, M. M., and O'Donnell, M. J., *J. Am. Chem. Soc.*, **74**, 1805 (1952).
(8) Schiedt, U., and Reinwein, H., *Z. Naturforschung*, **7b**, 270 (1952).
(9) Sands, J. D., and Turner, G. S., *Anal. Chem.*, **24**, 791 (1952).

Eastman Solvents for Spectrophotometry

These liquids are specially tested Eastman Organic Chemicals which are frequently used as solvents for spectrophotometry. Each lot is carefully controlled for high transmission and freedom from troublesome contaminants in the regions shown in the chart at the bottom of page 4. The catalogue numbers of the chemicals in this spectro grade are always identified with the prefix "S."

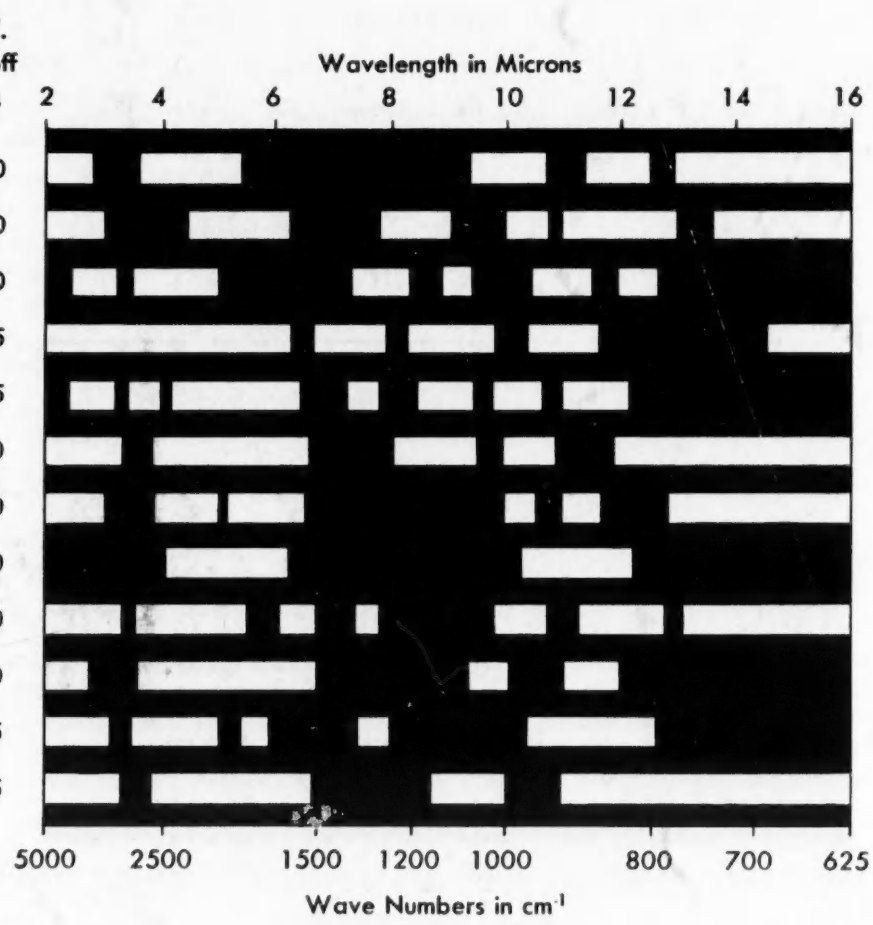
S	297	Acetone	500 cc.	$2.55	3 l.	$12.80
S	488	Acetonitrile	500 cc.	2.50	3 l.	12.50
S	777	Benzene	500 cc.	1.75	3 l.	8.00
S	444	Carbon Tetrachloride	500 cc.	1.35	3 l.	5.70
S	337	Chloroform	500 cc.	2.20	3 l.	10.70
S	702	Cyclohexane	500 cc.	5.00	3 l.	27.50

S 997	Ethyl Ether		640 cc.	$ 3.10
S 467	Methanol	500 cc. 2.55	3 l.	12.80
S 1227	Methyl Formate	500 cc. 1.25	3 l.	5.00
S 212	iso-Propyl Alcohol	500 cc. 1.35	3 l.	5.70
S 214	Pyridine		500 cc.	6.00
S 2396	2,2,4-Trimethylpentane		500 cc.	5.70

Chart of Spectrophotometric Solvents

The chart shown below should prove helpful to those who have occasion to use solvents for spectrophotometric work. The chart is 8½ x 11 inches in size, printed on cardboard, and suitable as a wall chart.

In it are given the areas of usefulness, in both ultraviolet and infrared regions, of the newly offered special spectro grade of Eastman Organic Chemicals. The ultraviolet cutoff is that wavelength at which the absorbance or optical density of a 1-cm layer approximates one. White areas in the background indicate wavelengths (or wave numbers) in the infrared where sufficiently high transmission in cells of the usual thickness is obtained to make them valuable for this work.

Copies of this chart may be obtained without charge from Eastman Organic Chemicals Dept., Distillation Products Industries, Rochester 3, N. Y.

		U.V. Cutoff mμ
S 297	Acetone	330
S 488	Acetonitrile	220
S 777	Benzene	280
S 444	Carbon Tetrachloride	265
S 337	Chloroform	245
S 702	Cyclohexane	210
S 997	Ethyl Ether	220
S 467	Methanol	210
S1227	Methyl Formate	260
S 212	iso-Propyl Alcohol	210
S 214	Pyridine	305
S2396	2,2,4-Trimethylpentane	215